

WE CLAIM:

1. A process for producing a dry image on a substrate, comprising the steps of:
 - (a) applying to the surface of a reflective, glossy, and/or luminescent substrate, to form an opaque coating thereon, an opaque coating composition comprising (i) a monomeric polybase and a monomeric polyacid, (ii) a polymeric polybase and a monomeric polyacid, (iii) a monomeric polybase and a polymeric polyacid, or (iv) a combination thereof; and
 - (b) contacting the coated substrate with a recording liquid that renders the opaque coating partially or entirely transparent.
2. The process of claim 1, wherein the image is a metallic-looking image.
3. The process of claim 1, wherein step (a) is repeated at least once, producing a multilayer coating on the substrate.
4. The process of claim 3, wherein at least two different opaque coating compositions are used in the repeated application steps (a).
5. The process of claim 1, wherein the opaque coating composition comprises a monomeric polybase and a monomeric polyacid.
6. The process of claim 5, wherein the monomeric polyacid has the structural formula (I)



wherein:

R is selected from the group consisting of alkyl, alkenyl, aryl of 1 to 3 rings which may be fused or linked, and 5- and 6-membered heterocyclic rings having from 1 to 3 heteroatoms selected from N, S and O;

L is an alkylene or alkenylene chain containing 1 to 8 carbon atoms;

x is 0 or 1;

y is an integer in the range of 2 to 10 inclusive; and

z is 1, 2 or 3,

with the provisos that (a) if w is 0 and x is 0, then y is 2 and z is 2, and (b) if z is 2 or 3, the distinct R groups are covalently linked to each other, and the monomeric polybase has the structural formula (II)



wherein R¹ and R² are hydrogen, alkyl, alkoxy, or hydroxyl-substituted alkoxy, and R, L, x, y and z are as defined with respect to the monomeric polyacid.

7. The process of claim 6, wherein the monomeric polyacid is selected from the group consisting of oxalic acid, maleic acid, succinic acid, methylsuccinic acid, malonic acid, adipic acid, glutaric acid, fumaric acid, dihydroxyfumaric acid, malic acid, mesaconic acid, itaconic acid, phthalic acid, isophthalic acid, terephthalic acid, 1,2-, 1,3- and 1,4-cyclohexane dicarboxylic acids, 1,2,3-cyclohexane tricarboxylic acid, 1,2,4-cyclohexane tricarboxylic acid, 1,3,5-cyclohexane tricarboxylic acid, 1,2- and 1,3-cyclopentane dicarboxylic acids, citric acid, tartaric acid, dihydroxyterephthalic acid, 1,2,3-, 1,2,4- and 1,2,5-benzene tricarboxylic acids, tricarballic acid, 1,2,4,5-benzene tetracarboxylic acid, norbornene tetracarboxylic acid, 3,3',4,4'-benzophenone tetracarboxylic acid, 1,2,3,4,5,6-benzene hexacarboxylic acid, aspartic acid, glutamic acid, and combinations thereof.

8. The process of claim 6, wherein the monomeric polybase is selected from the group consisting of ethylenediamine, 1,2-propane diamine, 1,3-propanediamine, 1,2,3-triaminopropane, *cis*-1,2-cyclohexanediamine, *trans*-1,2-cyclohexanediamine, 1,3-bis(aminomethyl)cyclohexane, *o*-, *m*- and *p*-phenylenediamine, tetramethyl *o*-, *m*- and *p*-phenylenediamine, hexamethylene-amine, hexamethylenetetraamine, diethylenetriamine, tetraethylenepentamine, pentaethylene-examine, pentamethyl diethylenetriamine, tris(2-aminoethyl)amine, 1,1,4,7,10,10-hexamethyl triethylenetetramine, tetramethyl-*p*-phenylenediamine, tetramethylethylenediamine, triethylenetetraamine, 4,4'-bipyridyl, and combinations thereof.

9. The process of claim 7, wherein the monomeric polybase is selected from the group consisting of ethylenediamine, 1,2-propane diamine, 1,3-propanediamine, 1,2,3-triaminopropane, *cis*-1,2-cyclohexanediamine, *trans*-1,2-cyclohexanediamine, 1,3-bis(aminomethyl)cyclohexane, *o*-, *m*- and *p*-phenylenediamine, tetramethyl *o*-, *m*- and *p*-phenylenediamine, hexamethylene-amine,

hexamethylenetetraamine, diethylenetriamine, tetraethylenepentamine, pentaethylene-examine, pentamethyl diethylenetriamine, tris(2-aminoethyl)amine, 1,1,4,7,10,10-hexamethyl triethylenetetramine, tetramethyl-*p*-phenylenediamine, tetramethylethylenediamine, triethylenetetraamine, 4,4'-bipyridyl, and combinations thereof.

10. The process of claim 1, wherein the opaque coating composition comprises a polymeric polybase and a monomeric polyacid.

11. The process of claim 10, wherein the monomeric polyacid has the structural formula (I)



wherein:

R is selected from the group consisting of alkyl, alkenyl, aryl of 1 to 3 rings which may be fused or linked, and 5- and 6-membered heterocyclic rings having from 1 to 3 heteroatoms selected from N, S and O;

L is an alkylene or alkenylene chain containing 1 to 8 carbon atoms;

x is 0 or 1;

y is an integer in the range of 2 to 10 inclusive; and

z is 1, 2 or 3,

with the provisos that (a) if w is 0 and x is 0, then y is 2 and z is 2, and (b) if z is 2 or 3, the distinct R groups are covalently linked to each other, and

the polymeric polybase comprises a nitrogenous polymer.

12. The process of claim 11, wherein the monomeric polyacid is selected from the group consisting of oxalic acid, maleic acid, succinic acid, methylsuccinic acid, malonic acid, adipic acid, glutaric acid, fumaric acid, dihydroxyfumaric acid, malic acid, mesaconic acid, itaconic acid, phthalic acid, isophthalic acid, terephthalic acid, 1,2-, 1,3- and 1,4-cyclohexane dicarboxylic acids, 1,2,3-cyclohexane tricarboxylic acid, 1,2,4-cyclohexane tricarboxylic acid, 1,3,5-cyclohexane tricarboxylic acid, 1,2- and 1,3-cyclopentane dicarboxylic acids, citric acid, tartaric acid, dihydroxyterephthalic acid, 1,2,3-, 1,2,4- and 1,2,5-benzene tricarboxylic acids, tricarballic acid, 1,2,4,5-benzene tetracarboxylic acid, norbornene tetracarboxylic acid, 3,3',4,4'-benzophenone tetracarboxylic acid, 1,2,3,4,5,6-benzene hexacarboxylic acid, aspartic acid, glutamic acid, and

combinations thereof.

13. The process of claim 11, wherein the polymeric polybase is selected from the group consisting of polyethyleneimine, polyvinylpyridine, polyallylamine (including N-alkylated and N,N-dialkylated polyallylamines), polyvinylaziridine, polyimidazole, polylysine, chitosan, poly(amino and alkylated amino)ethylenes, ethoxylated polyethyleneimine, propoxylated polyethyleneimine, and combinations thereof.

14. The process of claim 12, wherein the polymeric polybase is selected from the group consisting of polyethyleneimine, polyvinylpyridine, polyallylamine (including N-alkylated and N,N-dialkylated polyallylamines), polyvinylaziridine, polyimidazole, polylysine, chitosan, poly(amino and alkylated amino)ethylenes, ethoxylated polyethyleneimine, propoxylated polyethyleneimine, and combinations thereof.

15. The process of claim 1, wherein the opaque coating composition comprises a monomeric polybase and a polymeric polyacid.

16. The process of claim 15, wherein the polymeric polyacid is a carboxylic acid-containing polymer, and the monomeric polybase has the structural formula (II)



wherein:

R is selected from the group consisting of alkyl, alkenyl, aryl of 1 to 3 rings which may be fused or linked, and 5- and 6-membered heterocyclic rings having from 1 to 3 heteroatoms selected from N, S and O;

L is an alkylene or alkenylene chain containing 1 to 8 carbon atoms;

x is 0 or 1;

y is an integer in the range of 2 to 10 inclusive;

z is 1, 2 or 3; and

R¹ and R² are hydrogen, alkyl, alkoxy, or hydroxyl-substituted alkoxy,

with the provisos that (a) if w is 0 and x is 0, then y is 2 and z is 2, and (b) if z is 2 or 3, the distinct R groups are covalently linked to each other.

17. The process of claim 16, wherein the polymeric polyacid is selected from the group consisting of poly(acrylic acid), poly(acrylonitrile-acrylic acid), poly(styrene-acrylic acid), poly(butadiene-acrylonitrile acrylic acid), poly(butylacrylate-acrylic acid), poly(ethyl acrylate-acrylic acid), poly(ethylene-propylene-acrylic acid), poly(propylene-acrylic acid), alginic acid, phytic acid, and combinations thereof.

18. The process of claim 15, wherein the monomeric polybase is selected from the group consisting of ethylenediamine, 1,2-propane diamine, 1,3-propanediamine, 1,2,3-triaminopropane, *cis*-1,2-cyclohexanediamine, *trans*-1,2-cyclohexanediamine, 1,3-bis(aminomethyl)cyclohexane, *o*-, *m*- and *p*-phenylenediamine, tetramethyl *o*-, *m*- and *p*-phenylenediamine, hexamethylenediamine, hexamethylenetetraamine, diethylenetriamine, tetraethylenepentamine, pentaethylenehexamine, pentamethyl diethylenetriamine, tris(2-aminoethyl)amine, 1,1,4,7,10,10-hexamethyl triethylenetetramine, tetramethyl-*p*-phenylenediamine, tetramethylethylenediamine, triethylenetetraamine, 4,4'-bipyridyl, and combinations thereof.

19. The process of claim 16, wherein the monomeric polybase is selected from the group consisting of ethylenediamine, 1,2-propane diamine, 1,3-propanediamine, 1,2,3-triaminopropane, *cis*-1,2-cyclohexanediamine, *trans*-1,2-cyclohexanediamine, 1,3-bis(aminomethyl)cyclohexane, *o*-, *m*- and *p*-phenylenediamine, tetramethyl *o*-, *m*- and *p*-phenylenediamine, hexamethylenediamine, hexamethylenetetraamine, diethylenetriamine, tetraethylenepentamine, pentaethylenehexamine, pentamethyl diethylenetriamine, tris(2-aminoethyl)amine, 1,1,4,7,10,10-hexamethyl triethylenetetramine, tetramethyl-*p*-phenylenediamine, tetramethylethylenediamine, triethylenetetraamine, 4,4'-bipyridyl, and combinations thereof.

20. The process of claim 17, wherein the monomeric polybase is selected from the group consisting of ethylenediamine, 1,2-propane diamine, 1,3-propanediamine, 1,2,3-triaminopropane, *cis*-1,2-cyclohexanediamine, *trans*-1,2-cyclohexanediamine, 1,3-bis(aminomethyl)cyclohexane, *o*-, *m*- and *p*-phenylenediamine, tetramethyl *o*-, *m*- and *p*-phenylenediamine, hexamethylenediamine, hexamethylenetetraamine, diethylenetriamine, tetraethylenepentamine, pentaethylenehexamine, pentamethyl diethylenetriamine, tris(2-aminoethyl)amine, 1,1,4,7,10,10-hexamethyl triethylenetetramine,

tetramethyl-*p*-phenylenediamine, tetramethylethylenediamine, triethylenetetraamine, 4,4'-bipyridyl, and combinations thereof.

21. The process of claim 1, wherein the opaque coating composition is aqueous.
22. The process of claim 1, wherein the opaque coating composition further includes a film-forming binder.
23. The process of claim 1, wherein the opaque coating composition further includes a colorant.
24. The process of claim 23, wherein the colorant is a pigment.
25. The process of claim 24, wherein the pigment is selected from the group consisting of silica, titanium dioxide, calcium silicate and calcium carbonate.
26. The process of claim 23, wherein the colorant is a dye.
27. The process of claim 1, wherein the opaque coating agent represents approximately 5 wt.% to approximately 95 wt.% of the image-enhancing composition, based upon total solids weight of the composition after drying.
28. The process of claim 1, wherein the film-forming binder represents approximately 1 wt.% to approximately 40 wt.% of the opaque coating composition.
29. The process of claim 28, wherein the film-forming binder represents approximately 1 wt.% to approximately 50 wt.% of the opaque coating composition.
30. The process of claim 29, wherein the film-forming binder represents approximately 1 wt.% to approximately 15 wt.% of the opaque coating composition.
31. The process of claim 1, wherein the opaque coating composition further includes an optical brightener.

32. The process of claim 31, wherein the optical brightener represents approximately 0.01 wt.% to approximately 20 wt. % of the opaque coating composition.

33. The process of claim 1, wherein the opaque coating composition further includes a crosslinking agent.

34. The process of claim 33, wherein the crosslinking agent is ammonium zirconyl carbonate.

35. The process of claim 33, wherein the crosslinking agent is zirconium acetate.

36. The process of claim 1, wherein the surface of the substrate is reflective.

37. The process of claim 36, wherein the reflective surface is metallic.

38. The process of claim 36, wherein the substrate is a paper/foil laminate.

39. The process of claim 36, wherein the substrate is a metallized film.

40. The process of claim 1, wherein step (b) is performed using a writing instrument.

41. A substrate having a glossy, reflective, and/or luminescent surface coated with an opaque coating composition that becomes partially or entirely transparent upon contact with a recording liquid.

42. The coated substrate of claim 41, wherein the opaque coating composition comprises (i) a monomeric polybase and a monomeric polyacid, (ii) a polymeric polybase and a monomeric polyacid, (iii) a monomeric polybase and a polymeric polyacid, or (iv) a combination thereof.

43. The coated substrate of claim 41, wherein the substrate has a reflective surface.

44. The coated substrate of claim 43, wherein the reflective surface is metallic.

45. The coated substrate of claim 43, wherein the reflective surface is holographic.
46. The coated substrate of claim 41, wherein the substrate is comprised of a paper/foil laminate.
47. A process for producing an image comprising the steps of:
 - (a) printing an image on a reflective, glossy, and/or luminescent substrate;
 - (b) applying an opaque coating composition to the substrate, over the image, to form an opaque coating thereon; and
 - (c) contacting the coated substrate with a recording liquid that renders the opaque coating partially or entirely transparent.
48. The process of claim 47, wherein the opaque coating composition comprises (i) a monomeric polybase and a monomeric polyacid, (ii) a polymeric polybase and a monomeric polyacid, (iii) a monomeric polybase and a polymeric polyacid, or (iv) a combination thereof.
49. The process of claim 48, wherein the opaque coating composition further includes a colorant.
50. The process of claim 47, wherein the substrate has a reflective surface.
51. The process of claim 50, wherein the reflective surface is metallic.
52. The process of claim 50, wherein the reflective surface is holographic.
53. The process of claim 47, wherein the substrate is comprised of a paper/foil laminate.
54. The process of claim 47, wherein the substrate is comprised of a metallized film.
55. The process of claim 47, wherein step(c) is carried out using a writing instrument.
56. A light-emitting, reflective, and/or luminescent substrate coated with an opaque coating composition that becomes partially or entirely transparent upon contact with a recording liquid.

57. The substrate of claim 56, wherein the opaque coating composition comprises (i) a monomeric polybase and a monomeric polyacid, (ii) a polymeric polybase and a monomeric polyacid, (iii) a monomeric polybase and a polymeric polyacid, or (iv) a combination thereof.

58. The coated substrate of claim 56, wherein the substrate has a reflective surface.

59. The coated substrate of claim 58, wherein the reflective surface is metallic.

60. The coated substrate of claim 58, wherein the reflective surface is holographic.

61. The coated substrate of claim 58, wherein the substrate is comprised of a paper/foil laminate.

62. The coated substrate of claim 58, wherein the substrate is comprised of a metallized film.